

A New Humic Acid Preparation with Addition of Silver Nanoparticles

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Abstract Previously known biogenic stimulator humic acid (HA) was subjected in this study, and HA-based new preparation was developed by addition of silver (Ag) nanoparticles in its macromolecule. Extracted HA from healing mud was characterized and used as reducing agent for Ag ion as well as a stabilizer for Ag nanoparticles formed. Ethanol was utilized to precipitate the resultant product due to the stabilizer's (i.e., HA) analytical character and also to facilitate the reduction of Ag^+ to Ag^0 . The properties of the obtained hybrid composite were examined by XRD, UV, and FTIR spectroscopic techniques. The diameter of the nanoparticles in the HA polymer was up to 8.6 nm, and they were identified to be zero-valent Ag.

Keywords Composite • Healing mud • Humic acid • Silver nanoparticles

Introduction

Aromatic nucleus and functional groups in the HA molecule react with cell walls of organisms and with receptors in derma; furthermore, it shows a therapeutic effect by penetrating through tissues (Levitskii et al. 2001). HA has been found to be a major proportion of organic matters in Mongolian healing mud

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(Tserenpil et al. 2010), and it binds to organomineral particles. A hypothesis, therefore, was developed that HA from healing mud may possess a stabilizing character for metal nanoparticles as other natural polymers do (Abu Bakar et al. 2007; Adlim et al. 2004). Organic and inorganic hybrid composites bearing Ag nanoparticles are being synthesized and studied for different purposes. Moreover, the formation of Ag nanoparticles was examined in a variety of polymers (e.g., natural and synthetic) as size and dispersion pattern of metal particles were unique for each attempt. Humic substances from the healing mud differ from coal-, turf-, and soil-derived counterparts by their low molecular weight and high content of reactive functional groups. Thus, healing mud HA may provide more active sites for stabilization of metal nanoparticles.

Lipid, humic substances, and water extracts from healing mud widely used for therapy, among them HA-based products are commercially known. Therefore, we aimed to develop a method to obtain a new prospective HA preparation based on nanotechnology approaches. This new preparation may make it possible to resolve the disadvantages of conventional HA remedies by promoting biological activity, extending the duration of effectiveness, eliminating toxicity and side effects, as well as increasing the selective effect of treatments.

Materials and Methods

HA fraction was extracted from a sapropel peloid from Lake Gurvan Nuur (Khentii province, Mongolia) by the 0.2 N NaOH extraction. The alkaline extract was decanted, centrifuged, and then passed through a nuclear filter with a pore size of 1 μm to ensure the HA extract was free of clay particles. HA precipitated from the solution by acidification using 0.1 N HCl solution. For each set of experimental trials, 400 mg of peloid HA were dissolved in 6 mL of 1 N NaOH solution and heated for 15 min. AgNO_3 solutions with Ag concentrations ranging from 36 to 360 mg were added into the individual trials under constant stirring. Then the reaction mixture was filtered and ethanol added into it in order to precipitate the resultant product. Here, ethanol was used as an agent to facilitate $[\text{Ag}^+]$ reduction to Ag^0 and to precipitate the resultant product from the solutions. The peloid-derived HA and synthetic composites were studied by ultimate analysis, and their structures were investigated by using an FTIR spectroscopy, UV spectrometer, and XRD. In order to get quantitative results from the FTIR spectra, the intensities of the bands due to the oxygen containing functional groups were compared to those for aromatic ($1,619\text{ cm}^{-1}$) and aliphatic units ($2,920\text{ cm}^{-1}$) (Table 1). The Ag concentration was measured using an atomic adsorption spectrophotometer Perkin-Elmer Analyst 200.

Table 1 Comparison of band intensities in FTIR spectra of the peloid-derived HA

Functional groups and its corresponding wavelength (X_1/X_2)	Band intensity		Ratio of I_{X1}/I_{X2}
	(I_{X1})	(I_{X2})	
OH _{3,425} /C=C _{1,619}	44	52	0.84
Calk _{2,920} /C=C _{1,619}	52	52	1.00
CO _{1,228} /C=C _{1,619}	57	52	1.10
OH _{3,425} /Calk _{2,920}	44	52	0.85
CO _{1,228} /Calk _{2,920}	57	52	1.10

Results and Discussion

In this work, HA purification from clay particles was conducted efficiently using the nuclear filter and its ash content was negligible. It consisted of 48.9% C, 5.4% H, 5.0% N, and 1.3% Cl (percentages based on weight), and the molar ratio of H/C was 1.325, which indicates higher aliphaticity than typical value for other HA from coal and soil specimen as reported by the International Humic Substances Society. Ag content in the hybrid composites fluctuated from 5.5 g·100 g⁻¹ to 24.8 g·100 g⁻¹, where the initial ratio of Ag⁺:HA ranged between 1:1 and 1:11.

In FTIR spectrum, the peloid HA showed an intense band at 3,425 cm⁻¹ that was due to hydroxyl groups, and bands at 2,920 and 2,850 cm⁻¹ were attributed to the C–H of methyl and methylene groups. Bands at 1,619–1,591 and 1,379 cm⁻¹ were due to benzene ring with C=O units. The C–O in ether groups appeared at 1,228 cm⁻¹ and in hydrocarbons registered between 1,076 and 1,041 cm⁻¹. The FTIR spectra of the parent HA and hybrid composites were analogous, indicating that the HA molecular structure remained virtually unchanged after reaction. From Table 1, the parametrical calculation of HA structure from FTIR spectra revealed that the dominant oxygen-bearing moieties were hydroxyl groups of phenol and carbohydrate and carbonyls (C=O) of ether and carbohydrate. Therefore, the ratio of hydrophilic and hydrophobic moieties (OH_{3,425}/Calk_{2,920}) of HA was 0.85, while the ratio of aliphatic and aromatic (Calk_{2,920}/C=C_{1,619}) units was 1.

In the UV–vis spectrum of peloid-derived HA, an absorption maximum at 285 nm with high optic density was observed that was assigned to –OH groups in phenolic moiety (Fig. 1a). But in the HA/Ag spectrum (for trial 8), an absorption peak was observed at 424 nm (Fig. 1b) which is associated with the surface plasmon resonance of nanoparticles of metal Ag. This absorption maximum in the hybrid composite resulted from electron transmission in excited metals. It is believed that Ag ion was reduced in the presence of HA by its reducing sites (Struyk and Sposito 2001). An earlier published reference on HA/Ag composite was found, which studied it as a colorimetric sensor of herbicide (Dubas and Pimpan 2008); here, the average size of nanoparticles was 5 nm and the surface plasmon band appeared at around 400 nm. Similarly, study on Ag nanoparticle formation in the presence of various origins of HAs (i.e., the fresh water and marine sediment HAs) reported the surface plasma resonance peak at around 400–420 nm (Akaighe et al. 2011), and it was concluded that the aliphatic predominant HA (e.g., sedimentary) more readily

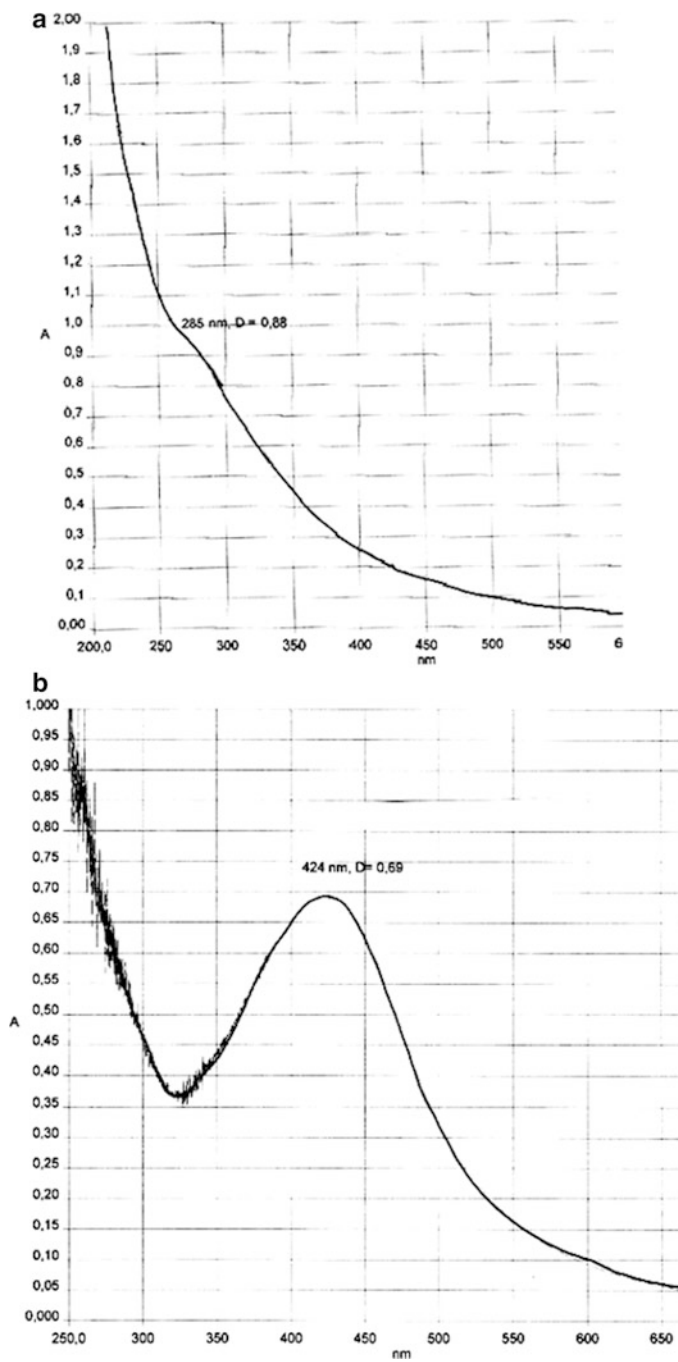


Fig. 1 UV-vis spectra of (a) HA in sodium hydroxide solution and (b) HA matrix contains Ag nanoparticles

reduced Ag^+ than did aromatic dominant HA (i.e., from soils) and formed Ag nanoparticles were stable. The variation in peak wavelength may result from particle size and agglomeration state of formed nanoparticles. The surface plasmon bands for nano-sized Ag formed in natural rubber matrix were ranged between 425 and 484 nm (Abu Bakar et al. 2007), while it was at about 418 nm for Ag/polyvinyl alcohol (Khanna et al. 2005) composite, where particles sizes were 4–10 nm and <10 nm, respectively.

The XRD spectrum was consistent with published data on nano-sized metal Ag (Alexandrova et al. 2006) and demonstrated the existence of Ag^0 in the product. All the prominent peaks at 2θ values of about 38, 44.2, 64.4, 77.6, and 81.60 represent the 111, 200, 220, 311, and 222 Bragg's reflections of Ag crystal. The diffraction line for the first precursor (i.e., Ag^+) was not observed, showing that the reduction process was completed. Also, the intensity distribution of diffraction line and distance between planes were in good agreement with the standard lines of Ag. Both UV–vis spectra and XRD analysis confirmed that the synthesized hybrid product contains Ag^0 . Here, reduction of Ag^+ could be induced by oxidation of phenolic hydroxyl and carbonyl groups in HA composition.

The average measure of region of coherent scattering and unit cell parameters of Ag nanoparticles were calculated by the 111 line, and α parameters of unit cell ranged 4.059 (1)–4.077 (1) \AA , and the average coherent scattering region of Ag nanoparticles was 8.6 nm in the HA/Ag composite. Aggregate resistant of colloidal system is defined by several parameters including small particles solvation and repulsion of electrical statistic force. It is certain that HA polyanions in aqueous solution react with positively charged Ag. This interaction could result in coagulation of the system. However, the colloid system was stable in the given ratios of HA:Ag. This showed that HA functional groups occupy all possible coordination positions on the surface of metal nanoparticles. HA associates to the nanoparticle surface and increases the hydrophilic character of products; this will sustain its stability in aqueous solution.

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